

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11)



EP 1 103 303 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
30.05.2001 Bulletin 2001/22

(51) Int Cl.7: B01J 31/40, C07C 45/78,
B01D 61/02, C07C 67/347

(21) Application number: 99203927.1

(22) Date of filing: 23.11.1999

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant: DSM N.V.
6411 TE Heerlen (NL)

(72) Inventors:

- Gelling, Onko Jan
6129 HV Stein (NL)
- Borman, Peter Cornelis
6163 LE Geleen (NL)

- Smits, Hubertus Adrianus
6212 GC Maastricht (NL)
- Cauwenberg, Veerle
3010 Leuven (BE)
- Vergossen, Franciscus Hendrik Paul
6104 AR Echt (NL)

(74) Representative: Kleiborn, Paul Erik et al
DSM Patents & Trademarks
Office Geleen
P.O. Box 9
6160 MA Geleen (NL)

(54) **Process to separate a rhodium/phosphite ligand complex and free phosphite ligand complex from a hydroformylation mixture**

(57) Process to separate a rhodium/phosphite ligand complex and free phosphite ligand from a hydroformylation mixture also containing high boiling hydroformylation compounds by contacting said mixture with a polymeric membrane, wherein said mixture is diluted with at least one diluent compound having a solubility parameter such that the absolute difference in relation to the solubility parameter of the membrane lies be-

tween 0 and $400\sqrt{kJ/m^3}$ and the ratio of the molar volume of the phosphite ligand and said diluent compound is ≥ 1.5 , to such an extent that the amount of high boiling compounds in said mixture is ≤ 50 wt.% and/or the amount of compounds with a molecular weight of between $x \pm 200$ is ≤ 20 wt.% whereby x is the cut-off of the membrane (g/mole) (relative to the total amount of the mixture).

EP 1 103 303 A1

Description

[0001] The invention relates to a process to separate a rhodium/phosphite ligand complex and free phosphite ligand from a hydroformylation mixture also containing high boiling hydroformylation compounds by contacting said mixture with a polymeric membrane.

[0002] With hydroformylation is meant the reaction of an ethylenically unsaturated organic compound with hydrogen and carbon monoxide in the presence of a hydroformylation catalyst, in which an aldehyde compound is obtained.

[0003] Compounds having a higher boiling point than the aldehyde product are designated as high boiling hydroformylation compounds in this specification. Examples are aldehyde condensation by-products, for example dimers, trimers and tetramers of the aldehyde.

[0004] A problem in hydroformylation processes is the excessive accumulation of such high boiling compounds in the recirculating catalyst stream. The recirculating catalyst stream is the stream which originates after the recovery of the hydroformylation aldehyde product. It is therefore necessary to separate the high boiling compounds from the recirculating catalyst stream by means of a purge. The presence of a high boiler purge has been found to be a problem because such purge is a potential source of rhodium loss. Rhodium metal is extremely expensive and significant losses can easily make the operation of commercial plants uneconomic. For a commercially interesting process it is therefore necessary to recover the catalyst system comprising the rhodium/phosphite ligand complex and free phosphite ligand from such a high boiler hydroformylation purge stream.

[0005] A process for separating rhodium and phosphite ligand from a mixture also containing high boiling hydroformylation compounds is described in WO-A-9634687. In Example 3 of this publication rhodium and a bidentate phosphite ligand is separated from a mixture containing rhodium, a bidentate phosphite ligand, butyraldehyde and 10 wt.-% trimer of butyraldehyde using a polydimethylsiloxane composite membrane obtained from Membrane Products Kiryat Weizmann. WO-A-9634687 does not exemplify the separation of rhodium and phosphite ligand from a high boiler hydroformylation purge.

[0006] It has been found that, when the membrane separation process as described in WO-A-9634687 is used for separating rhodium and phosphite ligand from a high boiler hydroformylation purge, the flux through the membrane is relatively small which prevents it from being a commercially attractive process.

[0007] The efficiency of a given membrane is determined by two parameters; its selectivity and the flow through the membrane. The latter, often denoted as the flux or permeation rate, is defined as the volume flowing through the membrane per unit area and time. The selectivity of a membrane towards a mixture is generally expressed by the retention R. The cut-off of a given membrane is defined as that molecular weight which is at least 90% rejected by the membrane. A membrane having a cut-off of x g/mole means that all compounds with a molecular weight greater than x are 90% or more rejected.

[0008] The object of the invention is to provide a membrane separation process for separating a rhodium/phosphite ligand complex and free phosphite ligand from a hydroformylation mixture also containing high boiling hydroformylation compounds with an improved flux.

[0009] This object is achieved in that said mixture is diluted with at least one diluent compound having a solubility parameter such that the absolute difference in relation to the solubility parameter of

[0010] the membrane lies between 0 and $400 \sqrt{\text{kJ/m}^3}$ and the ratio of the molar volume of the phosphite ligand and said diluent compound is ≥ 1.5 , to such an extent that the amount of high boiling compounds in said mixture is ≤ 50 wt.-% and/or the amount of compounds with a molecular weight of between $x \pm 200$ is ≤ 20 wt.-%, whereby x is the cut-off of the membrane (g/mole) (relative to the total amount of the mixture).

[0011] It has been found that with the process according to the invention the flux of the membrane separation process is increased more than proportional to the dilution factor. An advantage of the process according to the invention is that a smaller volume of area of membrane process equipment can be used. From an economical/investment point of view smaller process equipment is desired.

[0012] Dilution of the mixture which is fed to the membrane with a solvent is a technique known in the art for washing out low molecular weight compounds. This technique is called diafiltration. Dilution of 1 part of the feed with 1 part of solvent suggests that a double amount of membrane area is required in order to permeate the doubled amount of feed.

[0013] It has surprisingly been found that in the process according to the invention dilution of the feed with a factor x with at least one of the above mentioned diluent compounds advantageously results in an increase of the flux with a factor larger than x and hence results in a relative decrease of the membrane area required.

[0014] The diluent compounds used in the process according to the invention can be any compound having a solubility parameter such that the absolute difference in relation to the solubility parameter of the membrane lies between 0 and $400 \sqrt{\text{kJ/m}^3}$. The absolute difference between the solubility parameter of the diluent compound and the solubility parameter of the membrane is preferably between 0 and $300 \sqrt{\text{kJ/m}^3}$ and more preferably between 0 and $200 \sqrt{\text{kJ/m}^3}$. The ratio of the molar volume of the phosphite ligand and said diluent compound is preferably ≥ 3 , more preferably ≥ 5 .

[0015] The solubility parameter of the diluent compound, the aldehyde compound and the high boiling compounds

may be readily calculated according to the group contribution method described in AIChE J., 40(10), p. 1697-1710 (1994) "New Group Contribution Method for Estimating Properties of Pure Compounds", developed by L. Constantinou and R. Gani and Fluid Phase Equilibria, 103(1), p. 11-22 (1995), "Estimation of the Acentric Factor and the Liquid Molar Volume at 298K through a new group Contribution Method", developed by L. Constantinou, R. Gani, and J.P. O'Connell.

5 [0015] The solubility parameter of the membrane can be obtained from literature sources. Illustrative solubility parameters of various polymer membranes are given in WO-A-9634687.

[0016] The molar volume of the phosphite ligand and diluent compound may be calculated according to the above mentioned group contribution method described in Fluid Phase Equilibria, 103 (1), p. 11-22 (1995).

10 [0017] By free ligand is meant organophosphite ligand that is not complexed with (tied to or bound to) the rhodium atom of the complex catalyst. Examples of suitable phosphite ligands are given in WO-A-9634687 and WO-A-9733854.

[0018] In the process according to the invention the concentration of the high boiling compounds in the mixture which is fed to the membrane may not exceed 50 wt.%. Preferably the concentration of high boiling compounds is < 30 wt.%, more preferably \leq 25 wt.%.

15 [0019] The sum of the amounts of high boiling compounds, ethylenically unsaturated organic starting compound(s), aldehyde compound(s), diluent compound(s), rhodium/phosphite ligand complex, degradation products thereof and free phosphite ligand is 100 wt.%.

[0020] The concentration of the rhodium complex in the liquid to be treated is not critical. In a hydroformylation high boiler purge, the concentration will generally be higher than 25 ppm rhodium and lower than 3000 ppm rhodium. Preferably, the rhodium concentration is higher than 100 ppm and lower than 1200 ppm. More preferably, the rhodium concentration is equal to or higher than 200 ppm and equal to or lower than 800 ppm.

20 [0021] The high boiler hydroformylation mixture containing the hydroformylation catalyst and high boiling compounds will generally comprise also 25-80 wt.% of the aldehyde product and 0.5-5 wt.% ligand degradation products.

25 [0022] In the process according to the invention, a substantial portion of the high boiling compounds, diluent compound(s) and hydroformylation reaction product is passed through the membrane while retaining a substantial portion of the rhodium/phosphite ligand complex catalyst and free phosphite ligand. Thereafter high boiling compounds, diluent compound(s) and hydroformylation reaction product which passes through the membrane as permeate is removed for further downstream treatment and rhodium/phosphite ligand complex catalyst and free phosphite ligand is retained as a retentate and then recycled to the hydroformylation reactor.

30 [0023] The diluent compound(s) and the hydroformylation reaction product present in the permeate are separated in one or more separation steps according to conventional techniques. Advantageously the separation is performed using vacuum distillation.

[0024] The membrane used in the process according to the invention is chosen so that on bringing the mixture into contact with one side of the membrane at an applied pressure greater than the pressure on the opposite side of the membrane, the pressure differential being greater than the osmotic pressure of the system, the permeate has a reduced content of the rhodium/phosphite ligand complex. Suitable membranes include membranes which are stable in organic media, for example the polymeric composite membranes as for example described in WO-A-9634687. Preferred polymeric composite membranes are polydimethylsiloxane membranes as for example described in US-A-5265734.

35 [0025] The pressure of the feed stream of the membrane separation process according to the invention is generally between 0.1 and 4 MPa, preferably between 2 and 4 MPa. The process according to the present invention is performed using nano- or microfiltration. The pressure of the permeate is in general between 0.1 and 1 Mpa, preferably between 0.1 and 0.4 MPa.

40 [0026] The temperature of the polymeric membrane separation process according to the invention depends on the type of polymer used and is restricted by the temperature stability of the polymeric membrane. The temperature is generally between 10 and 50°C and preferably between 25 and 40°C.

45 [0027] The high boiler purge is generally removed continuously or intermittently from the hydroformylation system. The purge may be removed either directly from the reactor or, for example, from some point in the catalyst recycle stream.

[0028] The claimed process can be performed batchwise or continuously, in one or more stages.

50 [0029] With the one-step variant, the feed solution is added to the membrane under pressure. In the simplest case the permeate is drawn off and the concentrated solution is removed from the separating device as soon as the desired concentration has been reached. This procedure can also be performed continuously to increase the separating efficiency. The feed solution then flows along the membrane, is concentrated and continuously drawn off, as is the permeate.

55 [0030] Multi-stage separation is performed with separating stages either in parallel and/or in series. The series configuration, in which the concentrate is separated in every stage and the permeate solution is passed to the next separation stage, is especially advantageous for increasing the recovery of the rhodium/phosphite ligand complex and free phosphite.

[0031] The high boiler purge is preferably removed from a hydroformylation system for the preparation of a linear

EP 1 103 303 A1

(or terminal) aldehyde obtainable by hydroformylation of unsaturated olefins substituted with one or more functional groups according to formula (1) or (2) :



10 where R^9 and R^{10} are a hydrocarbon group or preferably hydrogen and R^{11} is a cyanide group or a hydrocarbon group, whether or not substituted with one or more functional groups which contain a hetero atom, for example oxygen, sulphur, nitrogen or phosphorus. Preferably, use is made of unsaturated olefins having between 4 and 20 carbon atoms according to formula (1) and/or (2), where R^9 and R^{10} are hydrogen.

[0032] Examples of unsaturated olefins having between 4 and 20 carbon atoms according to formula (1) and (2), where R⁹ and R¹⁰ are hydrogen, are 2-pentene nitrile, 3-pentene nitrile, 4-pentene nitrile, 4-pentenoic acid, 3-pentenoic acid and C₁-C₆-alkyl ester of 4-pentenoic acid and 3-pentenoic acid. The resulting aldehyde hydroformylation products, in particular methyl-5-formylvalerate, are intermediate products in the preparation of ϵ -caprolactam or adipic acid, which are in turn raw materials for the preparation of nylon-6 and nylon-6,6, respectively. Examples of C₁-C₆-alkyl-3-pentenoate esters and C₁-C₆-alkyl-4-pentenoate esters are methyl-, ethyl-, propyl-, isopropyl-, tert-butyl-, pentyl- and cyclohexyl-3-pentenoate and 4-pentenoate. Preferably, use is made of methyl-3-pentenoate, and/or methyl-4-pentenoate or of ethyl-4-pentenoate and/or ethyl-3-pentenoate because these compounds are readily obtainable. 3-pentene nitrile, 3-pentenoic acid and C₁-C₆-alkylesters of pentenoic acid may be present in the reaction mixture as a mixture which also comprises 2- and 4-pentenenitrile, 2- and 4-pentenoic acid and C₁-C₆-alkylesters of 2- and 4-pentenoic acid, respectively.

25 [0033] The process according to the invention will be described in more detail for the following preferred embodiments. It shall be evident that the below stated conditions will also be applicable for the above described starting mixtures in a manner clear to one skilled in the art.

[0034] A preferred embodiment is when the hydroformylation mixture which is treated in the process to the invention is derived from a hydroformylation process for the preparation of an alkyl 5-formylvalerate by reacting alkyl 3-pentenoate and/or alkyl 4-pentenoate with carbon monoxide and hydrogen using a rhodium/bidentate phosphite ligand complex catalyst as for example described in WO-A-9733854.

[0035] Examples of suitable diluent compounds in this preferred embodiment of the invention are the alkyl 5-formyl-valerate compounds and its isomers, alkyl 4-pentenoate and its isomers and alkyl valerate and mixtures containing at least two of these compounds. A preferred diluent compound is alkyl valerate or a mixture containing alkyl valerate and one or more alkyl pentenoate compound(s). It has been found that in this preferred embodiment dilution of the high boiler purge with alkyl valerate or with a mixture containing alkyl valerate and one or more alkyl pentenoate compounds is especially advantageous because this results in a further decrease of required membrane area. Another advantage of using alkyl valerate is that the retentate of the membrane separation process, containing rhodium/phosphite ligand complex, free phosphite ligand and diluent compound(s) can be recycled to the hydroformylation reactor without further treatment because alkyl valerate is formed as a by-product in the hydroformylation of alkyl-3-pentenoate and/or alkyl-4-pentenoate.

[0036] Alkyl valerate is a compound which can for example be formed through hydrogenation of the corresponding pentenoate compound. For example, methyl valerate is formed as a by-product when hydroformylating methyl-3-pentenoate and/or methyl-4-pentenoate into methyl-5-formylvalerate.

45 [0037] The process according to the invention is advantageously to be used in a process for the continuous preparation of an alkyl 5-formylvalerate by hydroformylating alkyl-3- and/or 4-pentenoate in the presence of a hydroformylation catalyst. First the alkyl 5-formylvalerate is separated from the rhodium/phosphite ligand complex catalyst in a conventional separation unit, for example using vacuum distillation, resulting in a fraction containing the alkyl 5-formylvalerate and a fraction containing the catalyst system and high boiling compounds.

50 Subsequently a part of the organic mixture containing the catalyst system and high boiling compounds is purged and the rhodium/phosphite ligand complex and free phosphite ligand are separated from the high boiling compounds with the process according to the invention and subsequently recycled to the reactor.

[0038] In this preferred embodiment of the invention the greatest part of the high boiling compounds has a molecular weight M_w of between 200 and

55 [0039] 1000. A typical distribution of the high boiling compounds is that 70% of all the high boiling compounds has a molecular weight less than 600, 25% has a molecular weight of between 600 and 1000 and 5% has a molecular weight more than 1000.

[0040] The molar ratio of the multidentate phosphite ligand to rhodium in the hydroformylation reaction mixture and the high boiler purge to be treated is generally from 0.5 to 100 and preferably from 1 to 10 and most preferably less than 1.2 (mol ligand/mol metal). Preferably the ratio is higher than 1.05. It has been found that in this range the ligand stability during hydroformylation is optimal and the loss of ligand in the high boiler purge according to this invention is minimal.

[0041] The invention is therefore also directed to a process to prepare alkyl 5-formylvalerate, wherein the following steps are performed:

- (a) hydroformylation of an alkyl-3- and/or 4-pentenoate in the presence of a catalyst system containing rhodium and a multidentate organic phosphite catalyst, whereby the hydroformylation reaction mixture contains 1-10, preferably 1.05-1.2 mol multidentate phosphite ligand per mol rhodium,
- (b) separating the catalyst system from the reaction mixture obtained in step (a) resulting in a fraction containing the linear and branched aldehyde compounds, unconverted starting compound and double-band isomers thereof and a fraction containing the catalyst system and high boiling compounds,
- (c) purging part of the fraction containing the catalyst system and high boiling compounds and recycling the rest to step (a),
- (d) separating the catalyst system from the purge with the process according to the invention,
- (e) reuse of the catalyst system obtained in step (d) in step (a),
- (f) separating the fraction containing linear and branched aldehyde compounds, unconverted starting compound and double-band isomers thereof obtained in step (b) in two or more separation steps in a fraction containing the linear aldehyde, a fraction containing the branched aldehyde compounds, a fraction containing the unconverted starting compound and double-band isomers thereof and a fraction containing at least alkyl valerate compound,
- (g) recycling the fraction containing the unconverted starting compound and double-band isomers thereof obtained in step (f) to step (a),
- (h) feeding at least a part of the fraction containing at least alkyl valerate compound to step (d).

[0042] The above described preferences regarding hydroformylation starting compound, conditions and catalyst system also apply here. Step (a) is preferably performed as described in for example US-A-5527950, EP-A-712828 or WO-A-9518089. Step (b) may be performed using any separation technique known to a person skilled in the art.

30 Examples of suitable separation techniques are (vacuum) distillation, crystallisation, extraction using a suitable extraction agent and membrane separation as for example described in WO-A-9634687.

[0043] A possible process according to the invention is schematically represented in Figure 1.

Figure 1 will be elucidated in a non-limitative manner below to illustrate the preparation of methyl-5-formylvalerate.

[0044] In Figure 1, methyl-3-pentenoate and/or methyl-4-pentenoate is fed to reactor (A) via stream (1). In Reactor 35 A the catalyst system is present. A mixture of CO and H₂ is fed to the reactor (A) via stream (2). The effluent of reactor (A) comprising methyl-5-formylvalerate, methyl-3-formylvalerate, methyl-4-formylvalerate, methyl-2-formylvalerate, low-boiling by-products (for example methyl valerate, methyl-2-pentenoate and methyl 4-pentenoate), high boiling compounds, any unconverted methyl-3-pentenoate, the catalyst system, carbon monoxide and hydrogen is fed to flasher 40 (B) via stream (3). In the flasher (B) the pressure is reduced to for example atmospheric pressure. Carbon monoxide and hydrogen are separated from the reaction mixture via stream (4) and recycled to the reactor (A). The resulting liquid mixture is fed to ion exchanger (C), a packed bed of a polystyrene matrix containing basic amine groups, via stream (5). The effluent is fed to separation step (D) via resulting liquid stream (6). In separation step (D) the catalyst system and high boiling compounds and some methyl-5-formylvalerate is separated from the liquid mixture (stream 45 7b). A part of stream (7b) is purged (stream (8)) and the rest is recycled to the reactor (A). The purge stream (8) is treated according to the process of present invention in the membrane separation unit (E) containing one or more 50 polymeric membranes in series and/or in parallel. The purge stream is somewhere in the membrane separation unit (E) diluted with at least one of the above mentioned diluent compounds. In the membrane separation unit (E) the diluted high-boiler purge is split into a concentrate stream (8a) and a permeate stream (8b). The concentrate containing catalyst system and free phosphite ligand is recycled to the reactor (A). The permeate stream (8b) containing methyl- 55 5-formylvalerate, methyl valerate and high boiling compounds is fed to separation step (F), preferably a vacuum distillation unit. In separation step (F) the liquid mixture is split into methyl valerate (stream 9a) and methyl-5-formylvalerate and high boiling compounds (stream 9b). The mixture containing methyl valerate (stream 9a) is optionally for at least a part fed to separation step (E). Stream (9b) is fed to separation step (G) in which methyl 5-formylvalerate (stream 10a) is separated from the high boiling compounds (stream 10b). Stream (7a), leaving the separation unit (D) contains the most of the volatile components, for example methyl-2-pentenoate, methyl-4-pentenoate, methylvalerate, most of the unconverted methyl-3-pentenoate and the most of the aldehyde products. Stream (7a) is fed to separation step H, preferably a vacuum distillation unit. In separation step H methyl-5-formylvalerate and its branched isomers are discharged via stream (11b). Stream (11b) is fed to separation step J, preferably a vacuum distillation unit. In separation

EP 1 103 303 A1

step J the branched methyl formyl valerates are discharged via stream (12a) and methyl-5-formyl valerate is discharged via stream (12b). Stream (11a) is fed to separation step (I), preferably a distillation unit. In separation step (I) methylvalerate, methyl-4-pentenoate and cismethyl-2-pentenoate are discharged via stream (13a). Stream (13a) is at least partially fed to separation step (E). Optionally the mixture of stream (13a) is treated with a hydrogenation catalyst in order to hydrogenate the methyl pentenoate compounds to methylvalerate. Trans-methyl-2-pentenoate and methyl-3-pentenoate are recirculated to reactor (A) via stream (13b).

[0045] The present invention also relates to a process for the separation of rhodium/phosphite ligand complex and free phosphite ligand from a hydroformylation reaction mixture, also containing aldehyde hydroformylation reaction product(s), ethylenically unsaturated starting compounds and optionally high boiling hydroformylation compounds in which the hydroformylation reaction mixture is contacted with an inorganic membrane. Suitable inorganic membranes are for example ceramic membranes formed from alumina, silica or zirconia. The use of inorganic membranes is advantageous because they exhibit superior thermal stability relative to polymeric membranes. The inorganic membrane separation process can therefore be operated at higher temperatures resulting in an improved flux through the membrane.

[0046] The invention will be elucidated by the following examples, however these are not intended to limit the scope of the invention in any way.

Comparative Experiment A

[0047] This experiment demonstrates that a low flux is obtained when the concentration of high boilers in the mixture is approximately 51 wt.%

[0048] In a continuous process according to figure 1, the hydroformylation substrate methyl-3-pentenoate is reacted with CO and H₂ to form a mixture of methyl formyl valerates. This is done by contacting methyl-3-pentenoate with a catalyst comprising Rh, a bidentate phosphite ligand ($M_w = 1090$) with formula (3) (molar ratio ligand/rhodium = 1.05-1.2 mol/mol) and a mixture of CO and H₂ (95°C, CO:H₂ = 1:1 mol/mol, P = 0.5 MPa, residence time = 6 hrs total in three well-mixed reactors in series). After partial separation of the products from the reaction mixture by vacuum evaporation, the stream containing the non-volatile catalyst is recycled continuously to the reactor section.

[0049] In this process the selectivity to high boilers is 0.2-1.5%. In this experiment the high boiler compounds which are formed are allowed to accumulate in the recirculating catalyst stream until their concentration is approximately 51 wt% (the remainder of the mixture comprises the catalyst system, degradation products thereof, reaction products and the hydroformylation substrate). The recirculating catalyst stream typically contains 360 ppm Rh (before dilution with a diluent compound). When the concentration of high boilers in the recirculating catalyst stream has reached 51 wt%, a desired amount of material is purged from the recirculating catalyst stream and is passed over a membrane MPF-50 (a polydimethylsiloxane composite membrane obtained from Membrane Products Kiryat Weizmann with solubility parameter $471 \sqrt{\text{kJ/m}^3}$ and a cut-off of 700 g/mole) of in an off-line membrane separation unit according to figure 2. The pressure on the retentate side is 0.3 MPa, the pressure on permeate side is approximately 0.5 MPa. The operating temperature is 27°C. The initial flux through the membrane is 0.74 kg/ (m²/hr) only and drops to lower values as the experiment is progressing.

EXAMPLE 1

[0050] Experiment A is repeated except that the high boiler hydroformylation purge mixture is diluted with various amounts of methylvalerate before contacting the purge mixture with the membrane. The solubility parameter of methylvalerate is $573 \sqrt{\text{kJ/m}^3}$. The difference in solubility parameter between the membrane and methylvalerate is $102 \sqrt{\text{kJ/m}^3}$. The molar volume of methylvalerate is 0.121 m³/kmol and the molar volume of the phosphite ligand with formula (3) is 0.932 m³/kmol. The ratio of the molar volume of the phosphite ligand and methylvalerate is 7.7.

[0051] Table 1 shows that dilution of the high boiler hydroformylation purge mixture with methylvalerate results in a flux improvement which is much larger than the dilution factor.

50

55

Table 1: Flux improvement by dilution with
methylvalerate

| concentration of high boilers [wt%] | flux [kg/m ² /hr] | flux improvement factor (1) | dilution factor (2) |
|---|---------------------------------|-----------------------------------|---------------------------|
| 22.4 | 9.2 | 12.5 | 2.2 |
| 24.2 | 6.0 | 8.1 | 2.1 |
| 25.5 | 8.1 | 10.9 | 2.0 |
| 27.4 | 6.6 | 8.9 | 1.8 |
| 29.3 | 5.0 | 6.8 | 1.7 |
| 29.4 | 4.7 | 6.4 | 1.7 |
| 30.4 | 5.4 | 7.3 | 1.6 |

(1) flux improvement factor = flux after
dilution/flux before dilution

(2) dilution factor = concentration of high boiling
compounds in the mixture before
dilution/concentration of high boiling compounds in
the mixture after dilution.

EXAMPLE 2

[0052] This example demonstrates that the separation process according to the invention can be carried out with good catalyst recovery and adequate high boiler removal in a very wide concentration factor⁽²⁾ range.

[0053] A mixture containing 25 wt% high boilers from the hydroformylation process described in experiment A is passed over the same membrane. Samples are taken on the retentate (concentrate) and permeate side of the membrane at three different concentration factors⁽²⁾. The Rh retention is given in Table 2.

EP 1 103 303 A1

Table 2: Rh retention vs. concentration factor

| [Rh] in concentrate (ppm) | [Rh] in permeate (ppm) | Rh retention (%) (1) | Conc. factor (-) (2) |
|---------------------------------|------------------------------|----------------------------|-------------------------|
| 171 | 13 | 92,4 | 1,03 |
| 829 | 55 | 93,4 | 4,79 |
| 1255 | 95 | 92,4 | 13,0 |

(1) Rh-retention = $(1 - [\text{Rh}] \text{ permeate} / [\text{Rh}] \text{ concentrate}) * 100\%$

(2) Concentration factor = Cf = initial mass of high boiler
containing mixture / mass of concentrate

[0054] Clearly, the retention is higher than 90% and constant for a very wide concentration factor range. The example also shows that by using a multi-stage membrane separation process, very high Rh-recovery (>99 %) can be obtained.

[0055] The retention of high boilers, catalyst complex and free ligand depends on the molar weight. The cut-off of the membrane used in these examples is 700 g/mole. This means that high boilers such as dimers and trimers of methyl-5-formylvalerate which have a molar weight \ll 700 g/mole will tend to permeate through the membrane, whereas very heavy high boilers and the catalyst complex and free ligand (molar weight \gg 700 g/mole) will accumulate in the concentrate. This is illustrated by Table 3 below.

35

40

45

50

55

Table 3: Concentration ratio's as a function
of molar weight for various concentration factors.

| Average Mw [g/mole] | Cf = 1.03 C(conc) / C(perm) | Cf = 4.79 C(conc) / C(perm) | Cf = 13.0 C(conc) / C(perm) |
|---------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 1296 | 5,00 | 10,50 | 14,67 |
| 1092 | 3,75 | 3,86 | 4,18 |
| 802 | 5,00 | 4,96 | 5,05 |
| 587 | 2,71 | 3,08 | 2,50 |
| 479 | 2,08 | 1,75 | 1,55 |
| 369 | 1,53 | 1,53 | 1,61 |
| 369 | 1,05 | 1,16 | 1,15 |
| 143 | 0,90 | 0,92 | 1,00 |
| 101 | 0,80 | 0,90 | 0,85 |

[0056] From Table 3 it is very clear that species with a low molar weight (< 700 g/mole) pass effectively through the membrane. It also shows that high molar weight species such as the catalyst complex and ligand (> 700 g/mole) are well retained by the membrane. Thus, the process is very effective in separating catalyst from high boilers with a molar weight < 700 g/mole.

Claims

1. Process to separate a rhodium/phosphite ligand complex and free phosphite ligand from a hydroformylation mixture also containing high boiling hydroformylation compounds by contacting said mixture with a polymeric membrane, characterized in that, said mixture is diluted with at least one diluent compound having a solubility parameter such that the absolute difference in relation to the solubility parameter of the membrane lies between 0 and $400 \text{ J}/\text{m}^3$ and the ratio of the molar volume of the phosphite ligand and said diluent compound is ≥ 1.5 , to such an extent that the amount of high boiling compounds in said mixture is < 50 wt.% and/or the amount of compounds with a molecular weight of between $x \pm 200$ is < 20 wt.% whereby x is the cut-off of the membrane (g/mole) (relative to the total amount of the mixture).
2. A process according to claim 1, characterized in that, the concentration of high boiling compounds is < 30 wt.%.
3. A process according to claim 2, characterized in that, the concentration of high boiling compounds is < 25 wt.%.
4. A process according to any one of claims 1-3, characterized in that the absolute difference between the solubility parameter of the diluent compound and the solubility parameter of the membrane is between 0 and $200 \text{ J}/\text{m}^3$.
5. A process according to any one of claims 1-4, characterized in that the ratio of the molar volume of the phosphite ligand and said diluent compound is ≥ 5 .
6. A process according to any one of claims 1-5, characterized in that, the hydroformylation mixture is derived from

EP 1 103 303 A1

a hydroformylation process for the preparation of an alkyl 5-formylvalerate by reacting alkyl 3-pentenoate and/or alkyl 4-pentenoate with carbon monoxide and hydrogen using a rhodium/bidentate phosphite ligand complex catalyst.

5 7. Process according to claim 6, characterized in that, the diluent compound is alkyl valerate or a mixture containing alkyl valerate and one or more alkyl pentenoate compounds.

8. Process for the preparation of an alkyl-5-formylvalerate, characterized in that, the following steps are performed:

10 (a) hydroformylation of an alkyl-3- and/or 4-pentenoate in the presence of a catalyst system containing rhodium and a multidentate organic phosphite catalyst, whereby the hydroformylation reaction mixture contains 1.05-1.2 mol multidentate phosphite ligand per mol rhodium,

(b) separating the catalyst system from the reaction mixture obtained in step (a) resulting in a fraction containing the linear and branched aldehyde compounds, unconverted starting compound and double-band isomers thereof and a fraction containing the catalyst system and high boiling compounds,

15 (c) purging part of the fraction containing the catalyst system and high boiling compounds and recycling the rest to step (a),

(d) separating the catalyst system from the purge with the process according to any one of claims 1-7,

(e) reuse of the catalyst system obtained in step (d) in step (a),

20 (f) separating the fraction containing linear and branched aldehyde compounds, unconverted starting compound and double-band isomers thereof obtained in step (b) in two or more separation steps in a fraction containing the linear aldehyde, a fraction containing the branched aldehyde compounds, a fraction containing the unconverted starting compound and double-band isomers thereof and a fraction containing at least alkyl valerate compound,

25 (g) recycling the fraction containing the unconverted starting compound and double-band isomers thereof obtained in step (f) to step (a),

(h) feeding at least a part of the fraction containing at least alkyl valerate compound to step (d).

30 9. A process for the separation of rhodium/phosphite ligand complex and free phosphite ligand from a hydroformylation reaction mixture, also containing aldehyde hydroformylation reaction product(s), ethylenically unsaturated starting compound(s) and optionally high boiling hydroformylation compounds, characterized in that, the hydroformylation reaction mixture is contacted with an inorganic membrane.

35

40

45

50

55

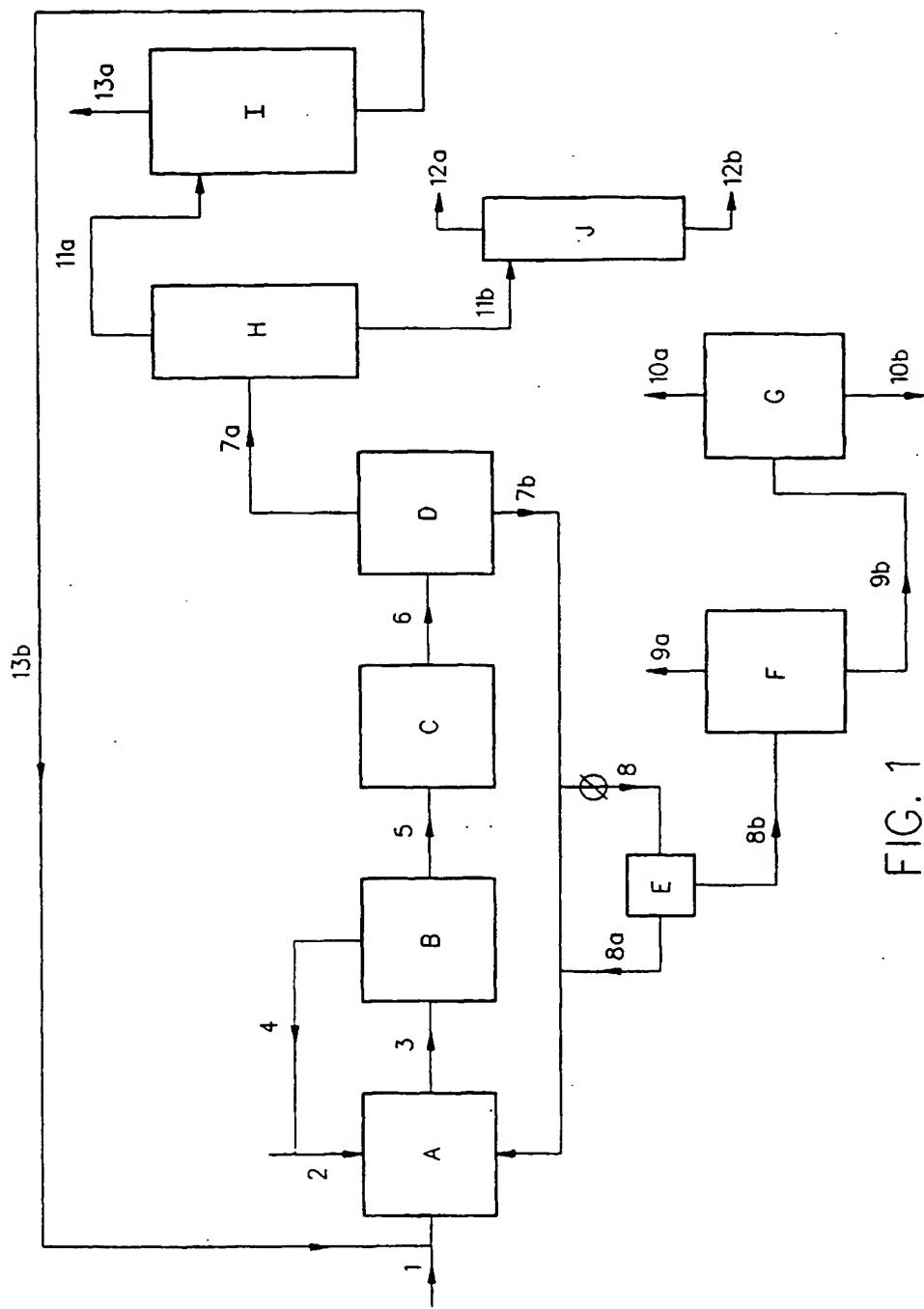


FIG. 1

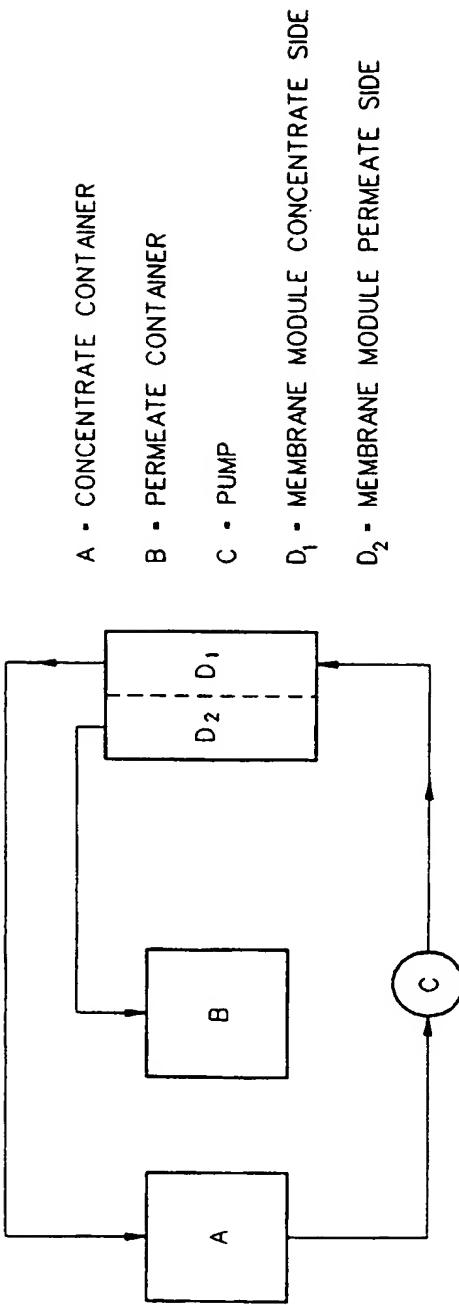


FIG. 2

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 20 3927

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|--|-------------------|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.) |
| D, X | WO 96 34687 A (UNION CARBIDE CHEM PLASTIC) 7 November 1996 (1996-11-07) | 9 | B01J31/40 C07C45/78 B01D61/02 C07C67/347 |
| A | * the whole document * | 1-5 | |
| X | EP 0 810 029 A (HOECHST AG) 3 December 1997 (1997-12-03) | 9 | |
| A | * claims 1-16 * * page 4, line 7 - line 15 * * page 8, line 20 - line 24 * | 1-5 | |
| A | GB 1 312 076 A (BP CHEM INT LTD) 4 April 1973 (1973-04-04) * the whole document * | 1-5, 9 | |
| A | EP 0 839 794 A (DSM NV) 6 May 1998 (1998-05-06) | 8 | |
| TECHNICAL FIELDS SEARCHED (Int.Cl.) | | | |
| B01D B01J C07C | | | |
| The present search report has been drawn up for all claims | | | |
| Place of search | Date of completion of the search | Examiner | |
| THE HAGUE | 13 April 2000 | Zuurdeeg, B | |
| CATEGORY OF CITED DOCUMENTS | | | |
| X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document | | | |
| T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | | | |

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 99 20 3927

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

13-04-2000

| Patent document cited in search report | | Publication date | Patent family member(s) | Publication date |
|--|---|------------------|---|--|
| WO 9634687 | A | 07-11-1996 | US 5681473 A BR 9508170 A CA 2193831 A EP 0781166 A IL 113999 A JP 10503425 T PL 318157 A | 28-10-1997 02-09-1997 07-11-1996 02-07-1997 17-08-1999 31-03-1998 12-05-1997 |
| EP 0810029 | A | 03-12-1997 | DE 19619527 A DE 19632602 A AU 2080397 A AU 713406 B AU 2080497 A AU 713496 B AU 2080597 A BR 9703078 A BR 9703083 A BR 9703095 A CA 2204675 A CA 2204676 A CA 2204818 A CN 1171981 A CN 1173484 A CN 1173485 A EP 0823282 A EP 0811424 A JP 10066877 A JP 2984233 B JP 10059890 A JP 2828169 B JP 10072395 A PL 319893 A PL 319894 A PL 319896 A RO 115025 A US 6020532 A US 5922634 A US 5773667 A US 5817884 A | 20-11-1997 19-02-1998 20-11-1997 02-12-1999 20-11-1997 02-12-1999 20-11-1997 10-11-1998 08-09-1998 08-09-1998 15-11-1997 15-11-1997 15-11-1997 04-02-1998 18-02-1998 18-02-1998 11-02-1998 10-12-1997 10-03-1998 29-11-1999 03-03-1998 25-11-1998 17-03-1998 24-11-1997 24-11-1997 24-11-1997 29-10-1999 01-02-2000 13-07-1999 30-06-1998 06-10-1998 |
| GB 1312076 | A | 04-04-1973 | NONE | |
| EP 0839794 | A | 06-05-1998 | AU 5883198 A EP 0937028 A WO 9819990 A | 29-05-1998 25-08-1999 14-05-1998 |

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82